Spectral Studies of Some Hydroxy-derivatives of Anthraquinones

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The u.v., visible, and i.r. spectra of several hydroxy-anthraquinones are discussed and the bands are assigned. These bands are compared with those of anthracene and anthraquinone. The band at 207 nm. is assigned to a n–σ^* transition; the bands at 252, 272, and 326 nm. are assigned by measuring spectra in solvents of various polarities. The stability constant for the 1,2-dihydroxyanthraquinone–ethanol complex is obtained.

THERE have been few investigations on the electronic spectra of quinones.[1-5] Morton and Earlam [1] showed that the position and type of substituents had a considerable effect on the absorption spectra, and Sheppard and Newsome [2] showed that the spectra were affected by the polarity of the solvent. Peters and Sumner [3] discussed the changes in spectra in terms of the electromeric effects of substituents in anthraquinones; the difference in the i.r. spectra of these compounds in sulphuric acid and oleum showed that they had a similar electronic structure in these solvents. Yoshida and Takabayashi [4] assigned all the bands in the spectra of anthraquinone and some derivatives to π–π^* transitions.

We have investigated the effect of the medium on the electronic transition of some di-, tri-, and tetra-hydroxy-anthraquinones. The effect on charge-transfer bands and on complex formation is also discussed. Stability constants for the complexes were determined where possible.

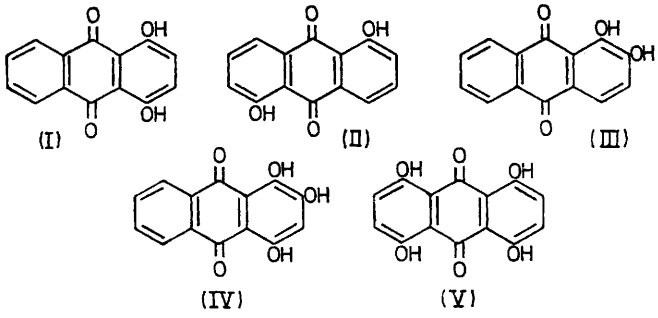
EXPERIMENTAL

1,4- (I) and 1,5-Dihydroxyanthraquinone (II) were prepared by the methods of Gatterman and Wielanel,[5] and Schwenk.[6] 1,2-Dihydroxy- (III), 1,2,4-trihydroxy- (IV), and 1,4,5,8-tetrahydroxy-anthraquinone (V) (B.D.H. reagents) were purified by recrystallisation or sublimation. Satisfactory analyses and m.p.s. were obtained. U.v., visible, and i.r. spectra were recorded with Unicam SP 800 and SP 200 instruments, respectively.

RESULTS AND DISCUSSION

On a localised picture, the hydroxy-anthraquinone should have characteristic bands due to electronic transitions of both the substituent and the anthraquinone nucleus. Since the transition energy of the substituent is usually high,[7] we have not considered this transition. The anthraquinone part of the molecule can be regarded as a 9,10-disubstituted anthracene; hence a comparison of the absorption spectrum of anthraquinone with that of anthracene could help in the assignment of bands corresponding to the quinonoid and benzenoid systems.

The absorption spectrum of anthraquinone in ethanol (Figure 1) has peaks at 207, 252, 272, and 326 nm. The peaks at 252, 272, and 326 nm. have been assigned previously to π–π^* transitions.[4] The lower intensity of the 207 nm. band compared with that of the 252 nm.



band and the blue shift as the polarity of the solvent increases (Figure 2), could be due to blocking of the carbonyl lone pair, so the 207 nm. band was assigned to a n–σ^* transition. The 252 nm. band is present in the spectra of anthracene and anthraquinone; it was assigned, therefore, to a π–π^* transition of the benzenoid

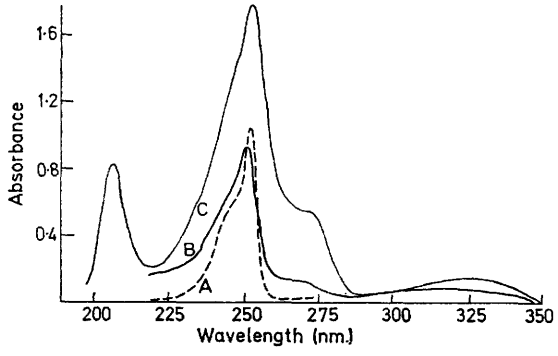


FIGURE 1 Absorption spectra of anthracene (A), anthraquinone in ethanol (B), and anthraquinone in ether (C)

system. The 272 and 326 nm. bands are absent from the spectrum of anthracene; hence they were assigned to quinonoid π–π^* transitions. They were further assigned to transition of the ethylenic and carbonyl system by measuring the spectra in solvents of various polarities.

The u.v. spectra of the hydroxy-compounds in ether (low polarity) (Figure 2) show separate bands due to the carbonyl and ethylenic systems, as in anthraquinone. Also, the 207 band shows a blue shift in more polar

[1] R. A. Morton and W. T. Earlam, *J. Chem. Soc.*, 1941, 159.
[2] S. E. Sheppard and P. T. Newsome, *J. Amer. Chem. Soc.*, 1942, **64**, 2937.
[3] R. H. Peters and H. H. Sumner, *J. Chem. Soc.*, 1953, 2101.
[4] Z. Yoshida and F. Takabayashi, *Tetrahedron*, 1968, **24**, 933.
[5] L. Gatterman and H. Wieland, 'Laboratory Methods of Organic Chemistry,' Macmillan, London, 1946.
[6] E. Schwenk, *J. prakt. Chem.*, 1921, **103**, 106.
[7] J. N. Murrell, 'The Theory of the Electronic Spectra of Organic Molecules,' Methuen, London, 1963.

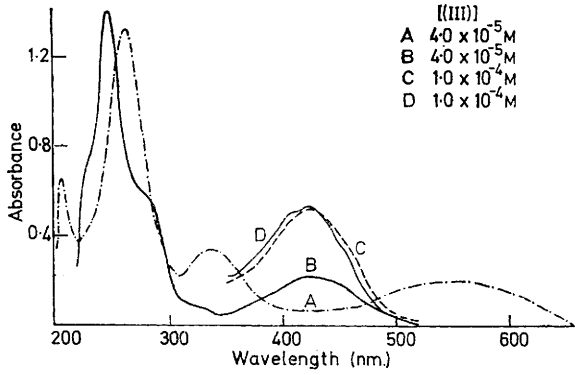
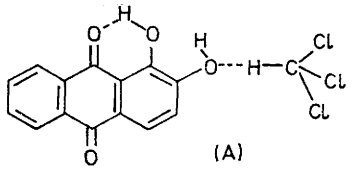


FIGURE 2 Absorption spectra of 1,2-dihydroxyanthracene (III) in ethanol (A), ether (B), acetone (C), and chloroform (D)

solvents. In chloroform, this may be due to a dipole–dipole interaction with the non-hydrogen bonded hydroxy-group [structure (A)].



(A)

The compounds (especially those with a non-hydrogen-bonded hydroxy-group) show a red shift (compared with 1,2-dihydroxyanthraquinone, is almost absent from the spectra of 1,4-di-, 1,5-di-, 1,2,4-tri-, and 1,4,5,8-tetra-hydroxyanthraquinone. In the latter compounds this may be due to blocking of the π electrons of the carbonyl groups, through hydrogen-bonding. However, the quinonoid bonds of the hydroxy-compounds in ether are nearly the same as those of anthraquinone. The proton acceptor nature of ethanol weakens the hydrogen bond between the hydroxy and carbonyl groups, so the transition energy of the n–σ^* and π–π^* bands is changed.

TABLE 1

Molar extinction coefficients ($\times 10^{-4}$) of the hydroxyanthraquinones at different wavelengths

	Ether			Ethanol			
Compound	252	275	326	210	252	275	326
(III)	3·20	1·55	0·25	1·45	2·70	2·50	0·80
(I)	5·70	1·83	0·33	1·35	2·10	0·80	0·25
(II)	2·37	1·27	0·07	0·60	0·68	0·40	0·10
(IV)	2·53	0·77	0·30	1·10	0·76	1·24	0·40
(V)	—	—	—	0·80	0·90	0·74	0·32

The red shift of the quinonoid bands in ethanol may be due to dissociation, which increases delocalisation through the quinonoid system. This is shown clearly in 1,2-di-, 1,2,4-tri-, and 1,4,5,8-tetra-hydroxyanthraquinone (Table 1) which have free hydroxy-groups. At high pH, conjugation of the carbonyl group with the quinonoid system in 1,4-dihydroxyanthraquinone will be reduced (Figure 3); dissociation of the 1- and 4-protons may lead to increased delocalisation.

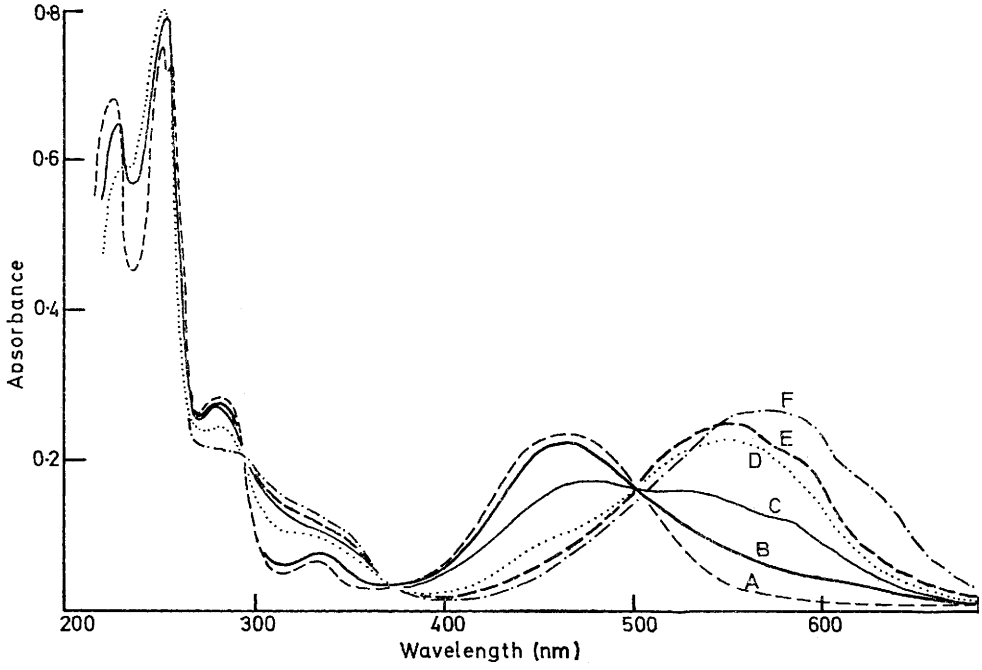


FIGURE 3 Absorption spectra of 1,4-dihydroxyanthraquinone ($2{\cdot}00 \times 10^{-5}$M) at different pH in aqueous solution: A, pH 6·6; B, 7·40; C, 8·35; D, 9·10; E, 10·10; and F, 11·30

The 326 nm. band is probably a π–π^* transition of the ethylenic system, since the 272 nm. band is almost

spectra in carbon tetrachloride) in solvents of high polarity, probably since solvent interaction with the hydroxy-group facilitates charge-transfer to the anthraquinone nucleus.

The 207 nm. band, of low intensity in the spectrum of

absent at high pH, and, furthermore, the intensity of the carbonyl band is lower in the i.r. spectra of the mono- and di-sodium salts of 1,4-dihydroxyanthraquinone, whereas the ethylenic band is not affected.

The existence of mesomeric structures may cause splitting of the benzonoid π–π^* transition at 252 nm.

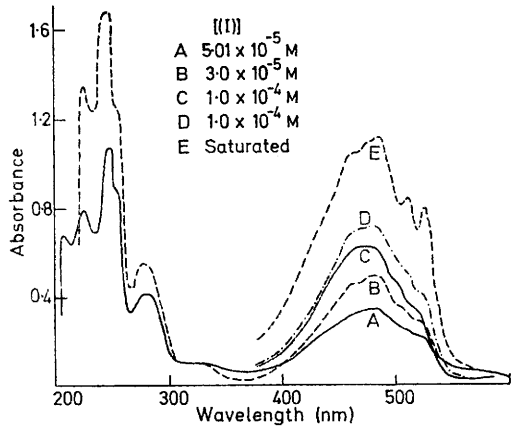
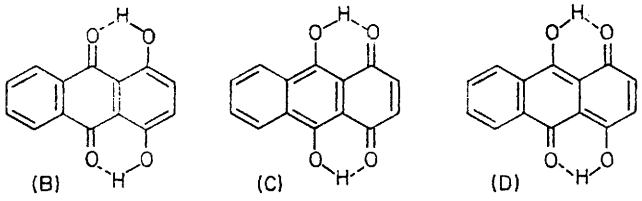


FIGURE 4 Absorption spectra of 1,4-dihydroxyanthraquinone (I) in ethanol (A), ether (B), acetone (C), chloroform (D), and carbon tetrachloride (E)

(Figure 4) and, for example, the three bands in the spectrum of 1,4-dihydroxyanthraquinone may be due to the structures (B)—(D).



The spectra of the hydroxyanthraquinones in nonpolar solvents show vibrational structure, which is decreased or absent in polar solvents, possibly owing to solvation.

The absorption spectra in the visible region show a single, intense, charge-transfer band (Table 2).

TABLE 2

$\lambda_{max.}$ (nm.) of the charge-transfer bands in different solvents

Compound	Solvent: Carbon tetrachloride	Ethanol	Acetone	Ether	Chloroform
(III)	430	555	430	430	410, 420
(I)	475	475	475	475	475
(II)	425	425	420	425	425
(IV)	480	525	480	480	480
(V)	485	560	485	485	485

Beer's law applied in all cases, indicating that solute–solute interactions were of minor importance compared with solute–solvent interactions (Figure 5) for the range of concentrations used.

The presence of an intermolecular hydrogen bond is further supported by the spectra in mixed solvents containing a nonpolar component (*e.g.* carbon tetrachloride)

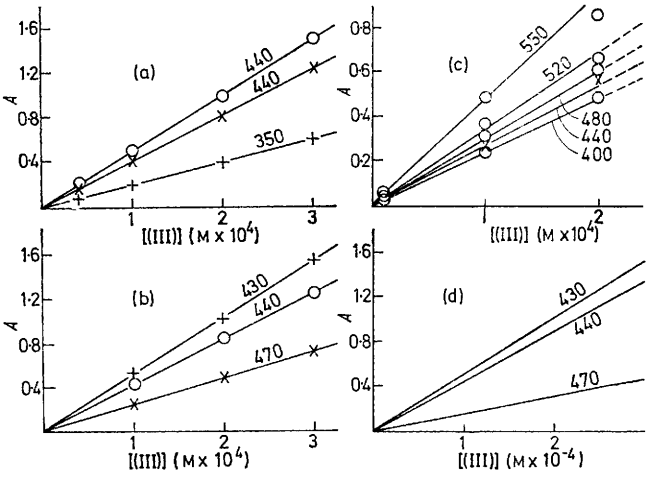
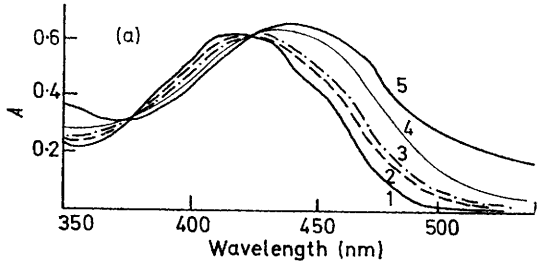


FIGURE 5 Variation of absorbance with concentration of 1,2-dihydroxyanthraquinone (III) in different solvents at different wavelengths (wavelengths in nm.); (A) in ether; (B) acetone, (C) ethanol, and (D) chloroform

and a proton acceptor (*e.g.* ethanol). Isobestic points were usually obtained when the concentration of the proton acceptor was varied at constant solute concentration



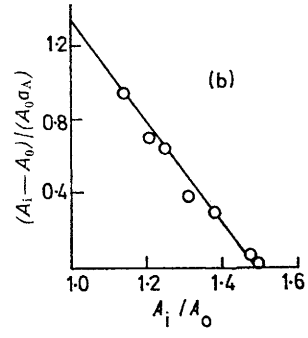


FIGURE 6 (a) Absorption spectra of 1,2-dihydroxyanthraquinone (1×10^{-4}M-solution in carbon tetrachloride) for different concentrations of ethanol, and (b) plot of $(A_i - A_0)/(A_0 a_A)$ for 1,2-dihydroxyanthraquinone at 450 nm.

(Figure 6), which indicates the existence of equilibrium (1) where D and A are the donor and acceptor, respec-

$$D + A \longrightarrow DA \qquad (1)$$

tively, and DA is a 1 : 1 complex. The stability constant is given by equation (2).

$$K = [DA]/[D] \,.\, [A] \qquad (2)$$

The effective concentrations of both A and D are given by equations (3a and b) where the concentrations referred

$$a_A = [A] + [DA] \qquad (3a)$$

$$a_D = [D] + [DA] \qquad (3b)$$

to are those at equilibrium.

The absorption at a given wavelength in a mixed solvent (A_i) is given by equation (4), where ε_0 and ε_i are molar extinction coefficients of D and DA, respectively, and l is the path length. The absorbance in an inert solvent (A_0) is given by equation (5).

$$A_i = l\varepsilon_0[D] + l\varepsilon_1[DA] \qquad (4)$$

$$A_0 = l\varepsilon_0 a_D \qquad (5)$$

Equation (6) can be derived from equations (2)—(5):

$$(A_i - A_0)/(A_0 a_A) = K\varepsilon_1/\varepsilon_0 - KA_i/A_0 \qquad (6)$$

If these assumptions are correct a plot of $(A_i - A_0)/(A_0 a_A)$ against A_i/A_0 should be linear, with slope $-K$ and intercept $K\varepsilon_1/\varepsilon_0$. Application of equation (6) to the 1,2-dihydroxyanthraquinone–ethanol system confirmed that a 1 : 1 complex was formed, with a stability constant of 2·6 (Figure 6).

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